Sulfoaluminate belite (SAB) cements from industrial by-products

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Phase composition of portland cement clinker

C-S-A-F ($CaO-SiO_2-Al_2O_3-Fe_2O_3$)

C_3S

C_2S

C_3A

C_4AF

Lime contents (%):

C_3S = 73.7 C_3A = 62.2

C_2S = 65.1 C_4AF = 46.2

Total lime content = 65-70%

Energy requirement for portland cement production

- Portland cement production is a highly energy consuming process
  - Clinkerization process takes place at about 1450^0C
  - Fuel energy = 3000 kJ/kg (2000 kJ/kg chemical reaction + 1000 kJ/kg heat losses) – major energy consumption is in the decarbonation process of calcite
  - Electrical energy = 110 kWh/t (396 kJ/kg ≈ 990 kJ/kg fuel energy) –major electrical energy consumptions are in clinker and raw material grinding

Phase composition of sulfoaluminate belite (SAB) clinker

C-S-A-F-$\bar{S}$ (CaO-SiO_2-Al_2O_3-Fe_2O_3-SO_3)

C_2S

$C_4A_3\bar{S}$

C_4AF

$C\bar{S}$

Lime contents:

C_2S = 65.1 $C_4A_3\bar{S}$ = 36.7

C_4AF = 46.2 $C\bar{S}$ = 41.2

Total lime content = 50-55% (40-45% lime from limestone)

Energy requirement for SAB cement production

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- Clinkerization process takes place at about 1200^{0}C
  - Fuel energy = significantly lower than 3000 kJ/kg

    (less lime to decarbonate + less heat losses)
  - Electrical energy = significantly lower than 110 kWh/t

    (processed or semi processed by-products + softer clinker)

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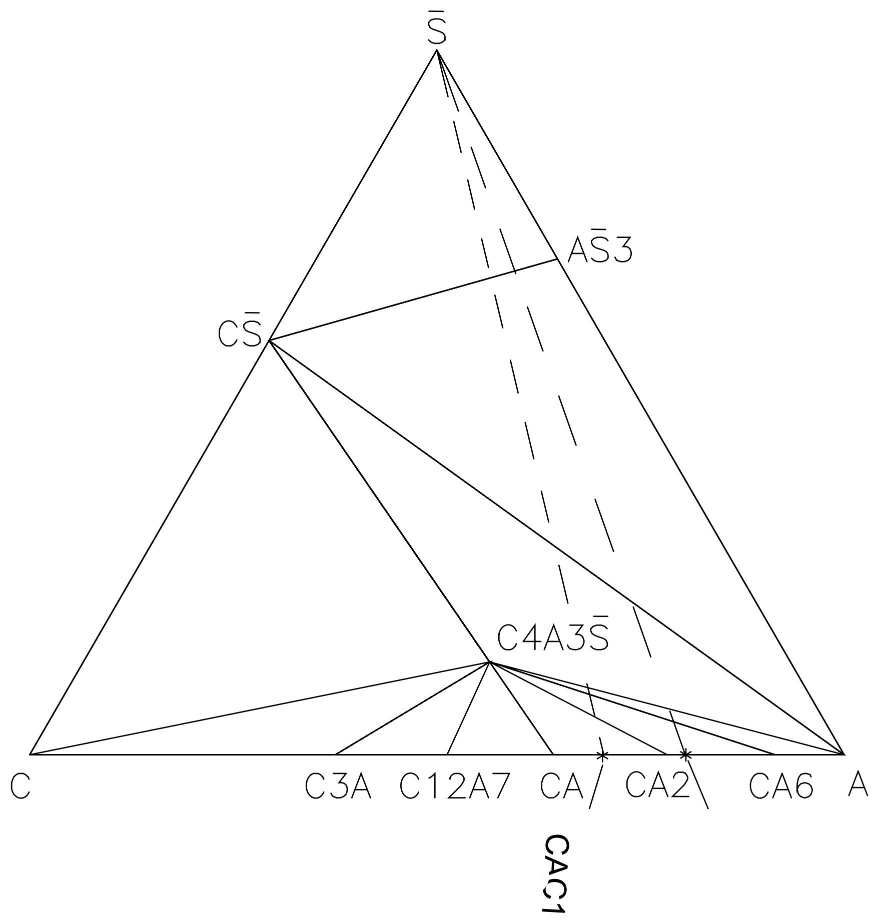
Phase compatibility in the system C-A-S*



Phase compatibility matrix

	Phases	1	2	3	4	5	6	7	8	9	10	11
1	C	_	0	1	1	1	1	1	0	0	1	1
2	C_3A		_	0	1	1	1	1	0	1	1	1
3	$C_{12}A_7$			_	0	1	1	1	0	1	1	1
4	CA				_	0	1	1	0	1	1	1
5	CA_2					_	0	1	0	1	1	1
6	CA_6						_	0	0	1	1	1
7	A							_	0	0	0	1
8	$C_4A_3S^*$								_	0	1	1
9	CS*									_	0	0
10	AS_3^*										_	0
11	S*											_

0 = compatible, 1 = not compatible

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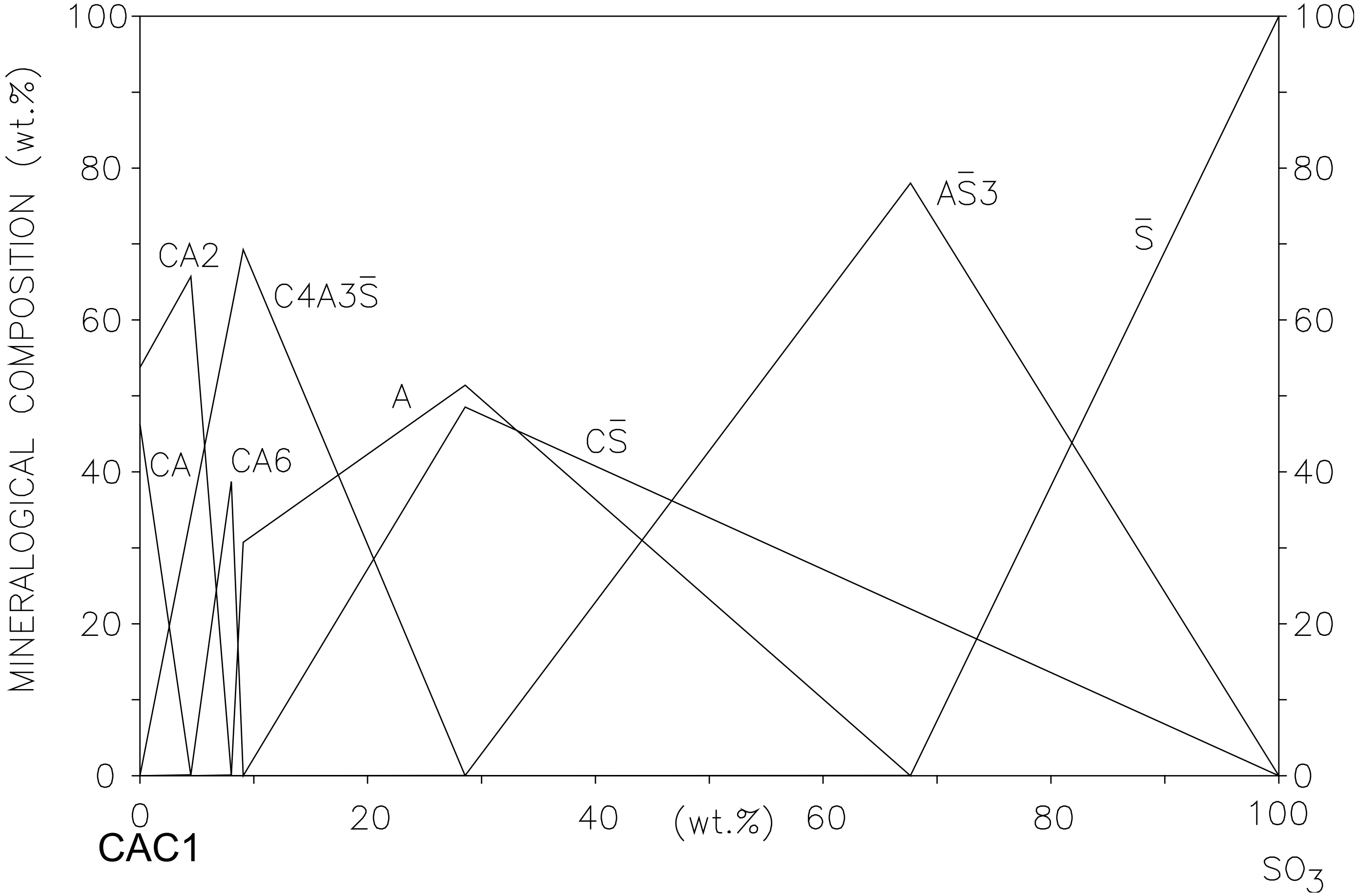
Phase assemblage in the system C-A-S*

1. $C-C_3A-C_4A_3S^*$
2. $C-C_4A_3S^*-CS^*$
3. $C_3A-C_{12}A_7-C_4A_3S^*$
4. $C_{12}A_7-CA-C_4A_3S^*$
5. $CA- CA_2-C_4A_3S^*$
6. $CA_2-CA_6-C_4A_3S^*$
7. $CA_6-A-C_4A_3S^*$
8. $A-C_4A_3S^*-CS^*$
9. $A-CS^*-AS_3^*$
10. $CS^*-AS_3^*-S^*$

Change in phase composition



Phase compatibility in the system C-S-A-S*

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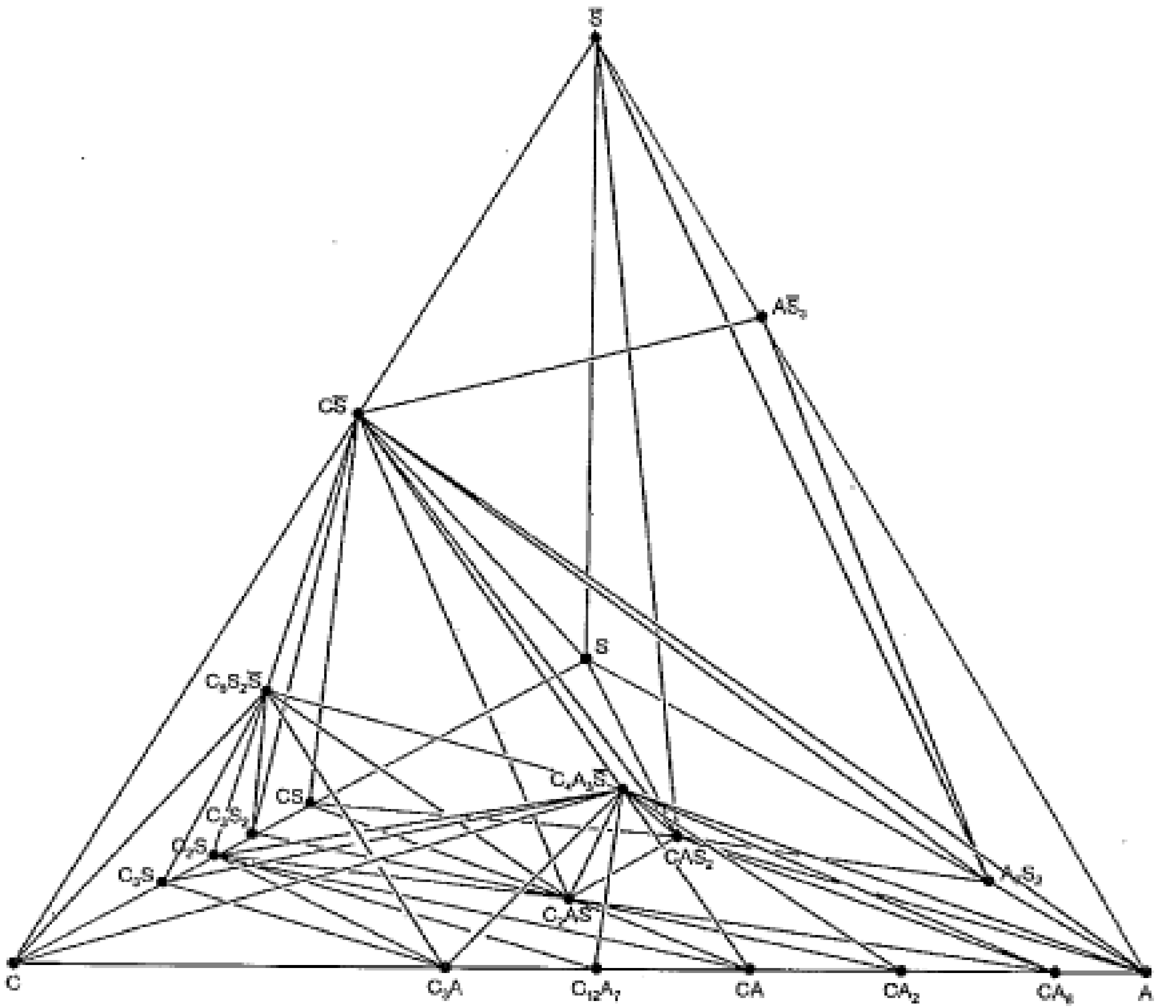

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Phase compatibility matrix in the system C-S-A-F-S* relevant to SAB cement

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	Phases	1	2	3	4	5	6	7	8	9	10	11	12	13	14
1	C_2S	_	0	0	0	0	0	0	0	0	0	0	0	0	0
2	C		_	1	0	1	1	0	1	1	0	1	1	0	0
3	C_3S_2			_	1	1	1	1	1	1	1	0	0	1	0
4	C_3A				_	0	1	1	1	1	0	1	1	0	1
5	$C_{12}A_7$					_	0	1	1	1	0	1	1	0	1
6	CA						_	1	0	0	0	1	0	0	1
7	C_2F							_	0	1	0	1	1	0	0
8	CF								_	0	0	1	1	0	0
9	CF_2									_	1	0	0	0	0
10	C_4AF										_	1	1	0	0
11	F											_	0	0	0
12	C_2AS												_	0	0
13	$C_4A_3S^*$													_	0
14	CS^*														_

0 = compatible, 1 = not compatible

$C_2S + CS^* \rightarrow C_5S_2S^*$ (stable 850 to 1100^{0}C)

$C + C_2S \rightarrow C_3S$ (above 1250^{0}C)

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Phase assemblage in the system C-S-A-F-S* relevant to SAB clinkers

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1. C_2S-C-C_3A-C_4AF-$C_4A_3S^*$
2. C_2S-C-C_2F-C_4AF-CS^*
3. C_2S-C-C_4AF-$C_4A_3S^*$-CS^*
4. C_2S-C_3S_2-F-C_2AS-CS^*
5. C_2S-C_3A-$C_{12}A_7$-C_4AF-$C_4A_3S^*$
6. C_2S-$C_{12}A_7$-CA-C_4AF-$C_4A_3S^*$
7. C_2S-CA-CF-CF_2-$C_4A_3S^*$
8. C_2S-CA-CF-C_4AF-$C_4A_3S^*$
9. C_2S-CA-CF_2-C_2AS-$C_4A_3S^*$

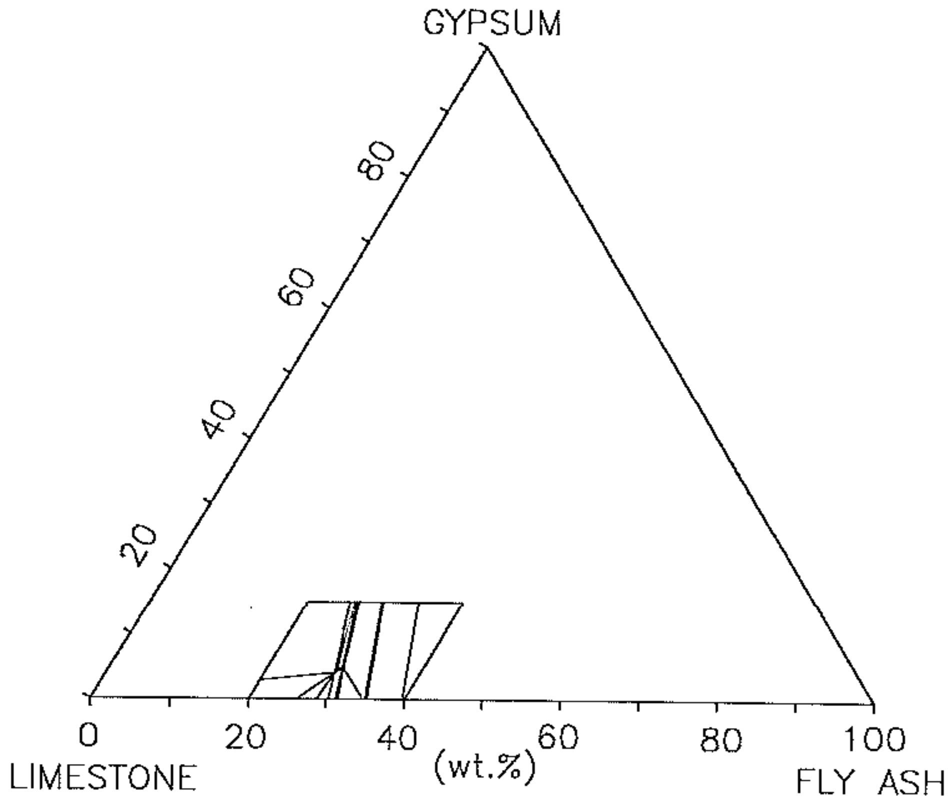
Phase assemblage in the system C-S-A-F-S* relevant to SAB clinkers

10. C_2S-C_2F-CF-$C_4A_3S^*$-CS^*
11. C_2S-C_2F-CF-$C_4A_3S^*$-CS^*
12. C_2S-C_2F-CF-$C_4A_3S^*$-CS^*
13. C_2S-CF-CF_2-$C_4A_3S^*$-CS^*
14. C_2S-CF_2-F-C_2AS-CS^*
15. C_2S-CF_2-F-C_2AS-CS^*
16. C_2S-CF_2-F-$C_4A_3S^*$-CS^*
17. C_2S-CF_2-C_2AS-$C_4A_3S^*$-CS^*
18. C_2S-F-C_2AS-$C_4A_3S^*$-CS^*

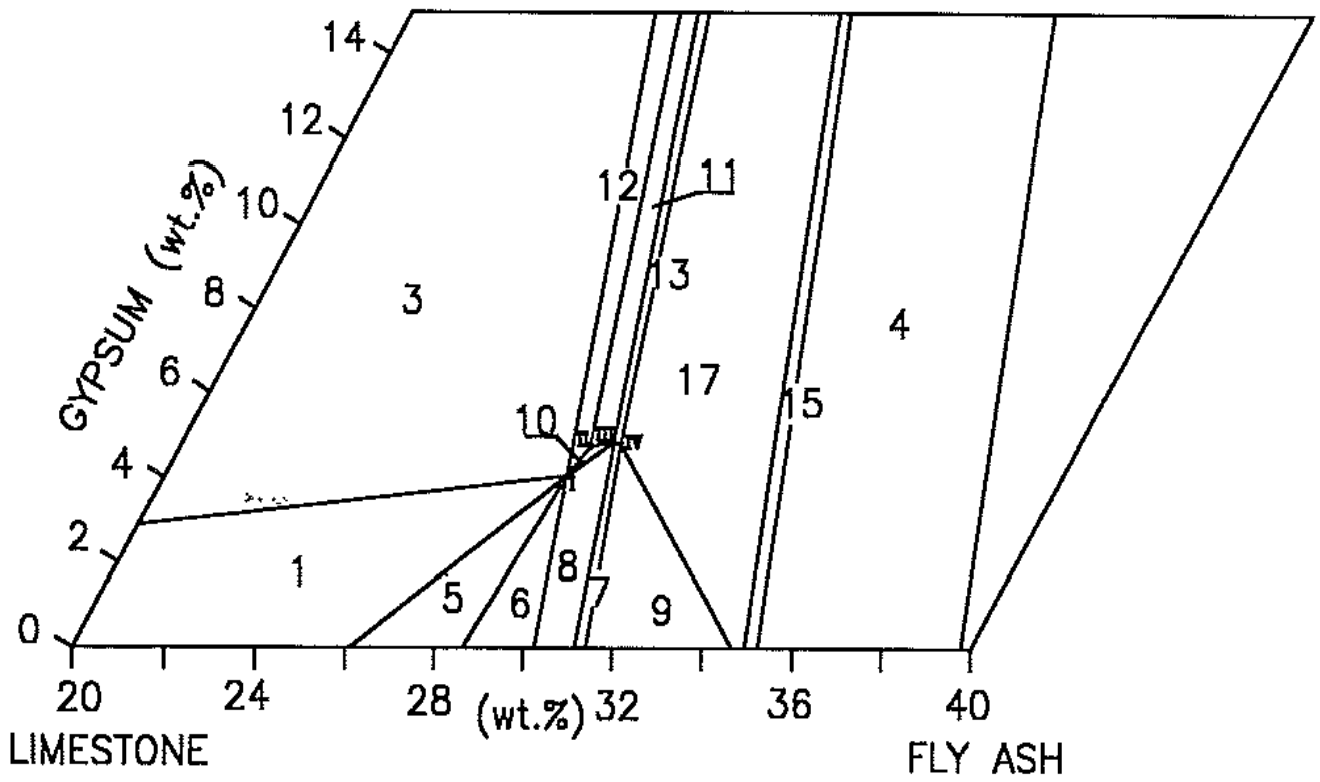
SAB primarily from by-products – (chemical composition of raw materials)

Oxides	Limestone	Fly ash	Gypsum
CaO	53.44	3.64	32.55
SiO_2	0.36	53.65	_
Al_2O_3	1.18	28.26	_
Fe_2O_3	0.08	7	_
SO_3	0.04	0.05	46.51
MgO	1.02	2.99	_
TiO_2	_	1.5	_
LOI	42.33	2.4	20.04

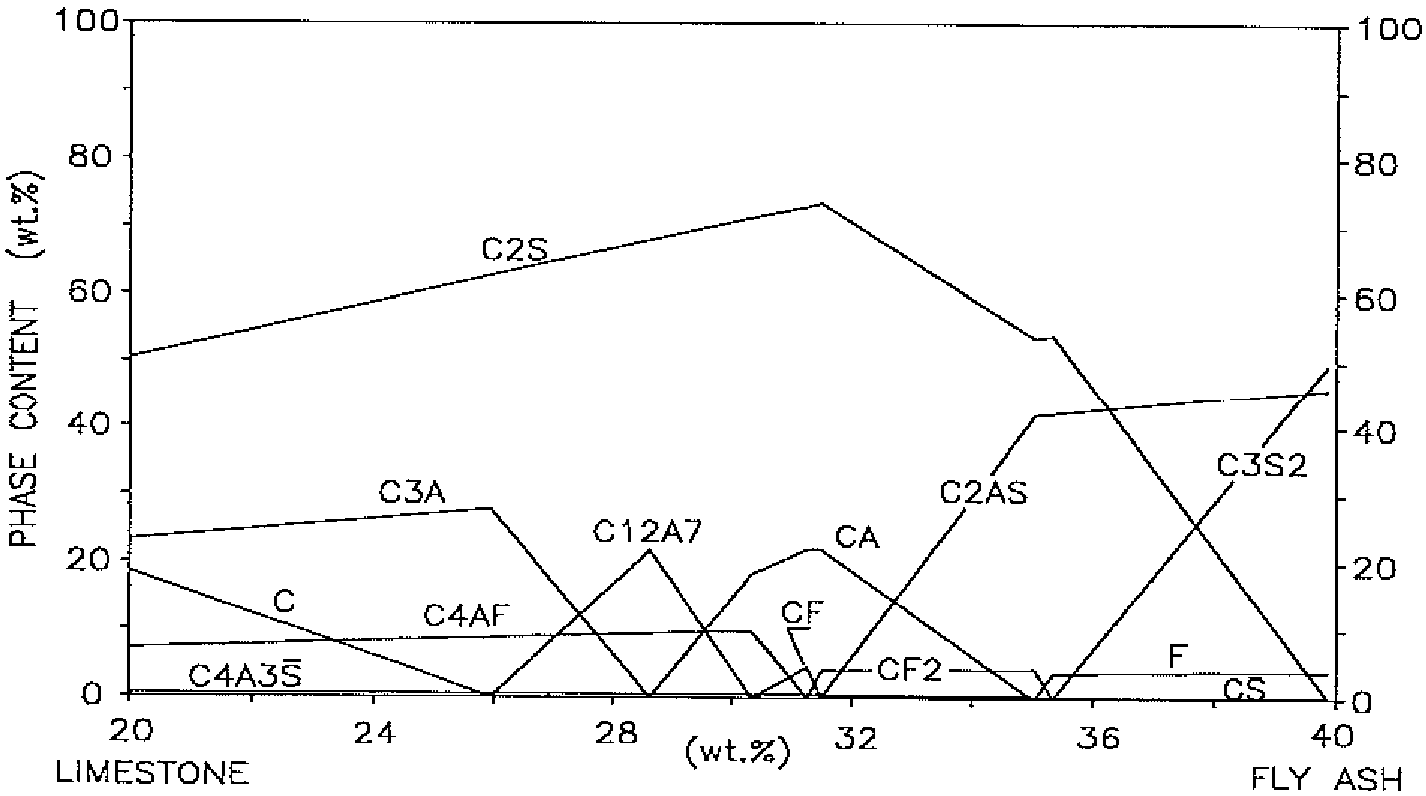
Ternary plot showing zone of SAB clinker



Phase field map of the system limestone - fly ash - gypsum



Change in phase composition in the system limestone-fly ash (no gypsum)



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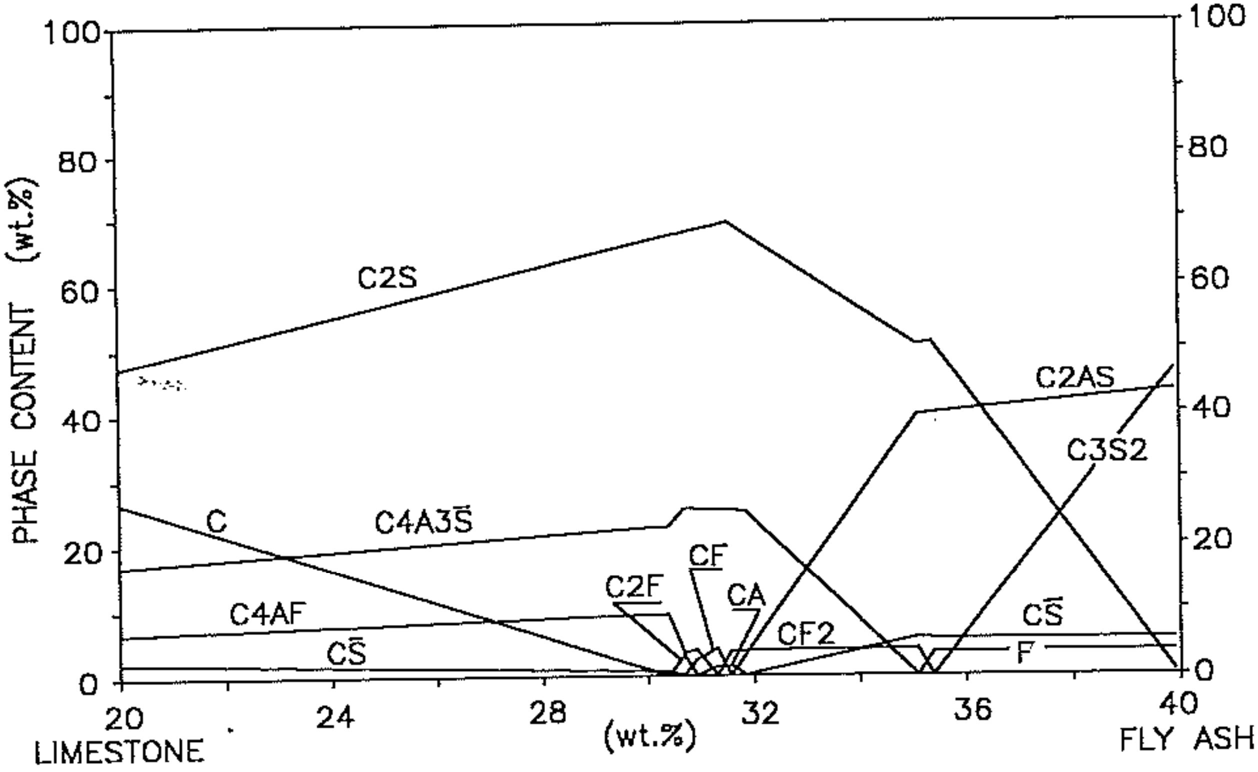
Change in phase composition in the system limestone-fly ash-gypsum (5%)



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Proportion of raw materials

Raw Mix No.	Limestone	Fly ash	Gypsum
1	71.0	14.0	15.0
2	76.5	17.5	15.0
3	65.0	20.0	15.0
4	63.5	16.5	20.0
5	60.0	20.0	20.0
6	57.5	22.5	20.0
7	64.0	14.0	25.0
8	57.5	17.5	25.0
9	55.0	20.0	25.0
10	65.0	15.0	20.0
11	62.0	13.0	25.0

Phase composition of cements

Cement No.	C2S	C	C4AF	CF2	C2AS	C4A3S*	CS*
1	45.2	23.8	6.8	0.0	0.0	14.8	9.5
2	52.4	14.0	7.8	0.0	0.0	16.9	8.8
3	57.4	7.4	8.5	0.0	0.0	18.4	12.8
4	52.7	10.0	8.0	0.0	0.0	16.4	12.8
5	59.6	1.0	8.8	0.0	0.0	18.4	12.0
6	56.5	0.0	0.0	3.7	12.5	14.6	12.7
7	50.0	10.1	7.7	0.0	0.0	15.0	17.0
8	57.0	1.1	8.6	0.0	0.0	17.0	16.2
9	54.0	0.0	0.0	3.6	12.3	13.3	16.8
10	49.7	14.4	7.5	0.0	0.0	15.5	13.2
11	48.0	12.8	7.4	0.0	0.0	14.4	17.3

Compressive strength of mortar specimen (MPa)

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Cement No.	1day	7 days	28 days
1	6.8	10.5	18.3
2	7.8	9	17.8
3	1.5	3	5
4	17.7	26.5	36.3
5	11.2	19	21.9
6	7.5	13	18.3
7	7.5	30.5	36.8
8	7.8	8.5	15
9	9.6	12.8	19.5
10	18.8	28	36
11	5	15.5	20

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Hydration reactions of SAB cements

$C_4A_3S^* + 6C + CS^* + 96\ H \rightarrow 3C_3A(CS^*)_3\ H_{32}$

$C_4A_3S^* + CS^* + 32\ H \rightarrow C_3A(CS^*)_3\ H_{32} + AH_3$

$C_2S + H \rightarrow C\text{-}S\text{-}H + CH$

$CH + AH_3 + CS^* + H \rightarrow C_3A(CS^*)_3\ H_{32}$

SAB cements using red mud

1. S. Sahu, "Preparation of Sulphoaluminate Belite Cement from Fly Ash and Red Mud", 4th NCB International Seminar on Cement and Building Materials, VIII-12 New Delhi, Dec. 11, (1994).
2. Singh, M., Upadhayay, S. N., and Prasad, P. M., "Preparation of Special Cements from Red Mud" Waste management, Vol 16, pp 665-670 (1996).

SAB cements using CFBC ash/ S-rich fly ash

1. Belz G. et al, “ Fludized Bed Combustion Waste as a Raw Mix Component for the Manufacture of Calcium Sulphoaluminate cements” (2005).
2. Bernardo, G. et al, “ Calcium sufoaluminate cements made from fludized bed combustion wastes” (2007).
3. Arjunan, P. et al, “Sulfoaluminate cement from low-calcium and sulfur-rich and other industrial by-products, CCR 29, 1305-1311 (1999).

SAB cements using slag

1. Ikeda, K. “ Cements along the join C_4A_3S* - C_2S”, 7th ICCC, III-31, Paris (1980).
2. Adolfsson, D., “ Steelmaking slags as raw material for sulphoaluminate belite cement” Ph. D. Thesis, Department of Chemical Engineering and Geosciences, Division of Process Metallurgy, Luleå University of Technology (2006).

Concluding Remarks

- Production of SAB cement can significantly reduce energy consumption compared to OPC.
- Use of processed or semi-processed by-products can further reduce the energy requirement.
- Phase compatibility data combined with mass balance equations can predict the phase assemblage of the cements with various raw mix proportion.
- This approach can be used to screen various raw materials for the suitability of SAB cement production.
- Cements with a wide range of properties can be produced.